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Title:

Rehydroxylation (RHX) Dating: Issues due to Short Term Elevated Temperature Events

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Abstract:

The long-term uptake of environmental moisture (rehydroxylation) is a property of fired clay ceramics. Rehydroxylation dating (RHX) attempts to provide age estimates for ceramics by measuring the associated mass gain and evaluating the duration over which this gain occurred. Simulations of the potential additional mass gained by fired clay ceramic brick and pottery due to short term (minutes to days) elevated temperature (>50°C) events, STETEs, and the effect this has on age estimations as part of rehydroxylation dating trials were explored. These events, including post-firing cooling of a brick, the use of pottery in cooking, and heating/cooling cycles during drying, for example, add considerable quantities of (re)hydroxyl mass to the sample and, particularly for samples with high activation energies (>130kJ/mol), the effect on age estimations can in some instances be detrimental (of the order of hundreds or thousands of years); where the activation energy is lower, the effects only become considerable at higher temperatures (e.g. >75°C) and over longer durations (days). Simulations of the STETEs for a brick cooling over a range of activation energies and for a variety of post-firing cooling durations and cooling temperature profiles, as well as for a pot undergoing varied numbers of cooking cycles (*stewing* and *boiling*) are presented, highlighting the magnitude of the issue if unaccounted for. STETEs are also shown to be a plausible major contributor to the age discrepancies (resulting in very old ages) between known and estimated ages in associated dating trials. The implications for RHX dating are discussed.

Keywords:

Rehydroxylation, Dating, Simulations, Temperature, Dependence, Discrepancies

1. Introduction

Rehydroxylation dating (RHX) was first proposed as a direct dating method for archaeological ceramics following investigations into the expansive properties of fired clay bricks (Wilson et al. 2003). When inorganic clays are fired at temperatures in the range 450-900°C hydroxyls of the clay minerals are converted to water and subsequently evaporated (dehydroxylation), accompanied by a collapse of the crystal structure of the clay (for example, Bellotto et al., 1995; Gualtieri and Ferrari 2006; Wang et al., 2002). Following cooling, a reversal of this process takes place in the hardened ceramic; water from the environment is absorbed and rehydroxylation occurs (for example, Heller et al., 1962; Muller et al., 2000; Shoval et al., 1991). Central to rehydroxylation dating are that (a) the rate at which rehydroxylation occurs can be described by a well-defined equation (a function of $time^{1/4}$), (b) the rate has an exponential (Arrhenius) temperature dependence, (c) reheating the ceramic to a sufficiently high temperature (e.g. > 500°C) for a sufficient duration will dehydroxylate or reset the mass of the ceramic to that of the as-fired state and (d) any subsequent mass gain will replicate the original mass gain following firing, provided the environmental conditions (temperature) are the same (Wilson et al., 2009, 2012). Using gravimetric techniques, rehydroxylation dating (Wilson et al., 2009, 2012) takes advantage of these properties. In principle, by weighing a sample of ceramic (under controlled environmental conditions) before and after reheating, the mass the ceramic has gained since it was originally (or last) fired can be estimated using suitable methods. Following reheating, measuring the mass gain of the sample as it ages in a controlled environment (with a temperature equivalent to that which the ceramic was effectively exposed to during its lifetime, the effective lifetime temperature, ELT), will permit the original rehydroxylation rate to be calculated. With these two quantities, the mass of rehydroxyls and the mass gain rate, the elapsed time since firing can then be calculated.

Despite the promising application of these principles by Wilson et al. (2009, 2012) to date bricks, tiles and pottery up to 2000 years old, there is a growing body of work that demonstrates significant issues with many aspects of the method: aside from the 11 samples dated by Wilson et al. (2009, 2012) age estimations from other works have been unsatisfactory (for example, Burakov and Nachasova 2013; Le Goff and Gallet 2015a; Numrich et al., 2015; Barrett 2017a); the $time^{1/4}$ model is inadequate (for example, Bowen et al., 2011, 2013; Le Goff and Gallet 2014, 2015a, 2015b; Barrett 2017a, 2017c) with the use of a $time^{1/n}$ model considered an improvement (for example, Bowen et al., 2011; Gallet and Le Goff, 2015; Le Goff and Gallet, 2015b; Barrett 2017a, 2017c); the presence of contaminants

(notably organics and gypsum) that interfere with rehydroxyl mass estimation are also an issue (Numrich et al., 2015; Barrett 2017b). Along with other experimental difficulties (for example Bowen et al., 2011; Zhao et al., 2015), questions surrounding the validity of successful dating trials have also arisen (Le Goff and Gallet, 2015a, 2015b; see also the review of Barrett 2015).

Little attention has been given to potential problems that arise when a ceramic is exposed to high temperatures ($>50^{\circ}\text{C}$) for short durations (minutes to days), referred to here as short term elevated temperature events (STETEs). Due to the Arrhenius temperature dependence of the rehydroxylation mass gain rate (Wilson 2009; Barrett 2013; Clelland 2014), a ceramic can gain exponentially greater quantities of mass at higher temperatures. The implications of this for RHX dating have previously been explored both in terms of how diurnal and annual temperature cycles can require corrections to age estimations if a mean lifetime temperature is used (Barrett 2011), and in terms of estimating an effective lifetime temperature (ELT) which reflects the average mass gain rate the ceramic will have had during its lifetime (Hall et al. 2013). Barrett (2013) demonstrated that for small bulk samples (30-40g) the mass gained during the cooling period following heating is quite significant and results in a curvature (non-linearity) in the mass gain data as a function of $t^{1/4}$ (applicable to $t^{1/n}$ also); this additional mass gain (i.e. above what would be expected for aging at ambient laboratory conditions alone) was shown to be equivalent to an apparent increase (equivalent to a *time-offset*) in the estimated age of the ceramic if ambient temperature alone was used in age estimation. However, this work did not consider in any detail the implications of this effect on dating trials.

The RHX age estimation, t_{age} , requires an estimate of the quantity of mass the ceramic has gained over its lifetime due to rehydroxylation and an estimate of the ELT the ceramic has experienced. The ELT is calculated using a constructed temperature history of the ceramic and an understanding of how the mass gain rate varies with temperature (see Hall et al. 2013). However, for long temperature histories (hundreds to thousands of years) there is the potential for minor temperature events, occurring on the order of minutes to days, to be overlooked; yet because of the exponential temperature dependence of the mass gain rate it is plausible that a considerable quantity of mass could be gained at high temperatures during such short events. Consequently, the effective lifetime temperature needs to be raised, otherwise age calculations will be overestimated. For example, with a piece of structural brick located on an external exposed face of a building since manufacture, this effective lifetime temperature may be expected to largely reflect local air temperatures; however immediately post-firing the brick may have experienced a considerable period of

cooling down (e.g. several days for a downdraught kiln, Brunswick 1990) during which accelerated mass gain can occur. For pottery that is used in cooking, repeated cycles of heating and cooling might also increase the effective lifetime temperature. Also overlooked is the potential mass gained by the ceramic while heating up and subsequently cooling as part of the drying stage of the RHX methodology.

To examine potential STETE effects on RHX age estimations, simulations of the mass gain due to varied brick cooling durations following initial firing, and also for pots undergoing varied cooking cycles (*stewing* and *boiling*), are conducted for a range of activation energies (and cooking cycles for pots). The effect this additional mass has on age estimations where the ELT is not altered to account for the STETE is examined and discussed.

The work also examines the possible effects of a range of STETEs experienced by post-medieval brick samples used in a recent dating trial (Barrett 2015). These events cover lifetime use events (post-firing cooling) and RHX methodology events associated with drying. Simulations of the lifetime mass gain by the ceramics without STETEs considered and with STETEs considered are generated. The potential additional age due to STETEs are then used to examine possible discrepancies in ages estimates obtained in the dating trial.

2. Theory and Method

2.1 Theory

After firing of a clay and its conversion to a hard ceramic (or subsequent reheating above 500°C), the ceramic gains mass in two stages (Savage et al. 2008a), *Stage 1* and *Stage 2*. The initial and more rapid *Stage 1* can be largely attributed to physisorption processes (the processes responsible for *Stage 2* are on-going and a lesser contributor to *Stage 1*) and has generally reached completion within 24 hours (Barrett 2017c). The prolonged and indefinite second stage, *Stage 2*, is likely due to both chemisorption and rehydroxylation processes (Gallet and Le Goff 2015, Barrett 2017c). The rate at which chemisorption/rehydroxylation takes place in *Stage 2* is well described by a $time^{1/n}$ (e.g. Bowen et al. 2011; Le Goff and Gallet 2014; Barrett 2015; 2017c) power law of the general form:

$$m(t) = a(T)t^{\frac{1}{n}} + m_0 \quad (1)$$

with $m(t)$ the sample mass, t the time since heating, m_0 the intercept mass of the $S2$ mass gain, a the mass gain rate (T is the *aging* temperature, i.e. the environmental temperature to which the ceramic is exposed and at equilibrium with). A fixed value of $1/n = 4$ was originally proposed and applied with some success (Wilson et al. 2009; 2012) but this has been increasingly shown to be unsatisfactory (e.g. Bowen et al. 2011; Le Goff and Gallet 2014; 2015a; 2015b; Barrett 2015; 2017c) with $1/n$ instead observed to be sample dependent and varying between 1/6-1/2 (e.g. Le Goff and Gallet 2014; Barrett 2017c).

The mass gain rate exhibits an exponential (Arrhenius) temperature dependence (Wilson et al. 2009). This can be described by the following equation (generalized from Hall and Hoff 2012; Hall et al. 2013):

$$a(T) = Ae^{-\frac{E_a}{nRT}} \quad (2)$$

with A the pre-exponential factor, E_a the activation energy, R the gas constant, T the temperature, and $n = 4$ for $t^{1/4}$ model.

If the mass gain rate can be estimated for a range of aging temperatures, the activation energy can be calculated from:

$$\ln\left(\frac{a}{a_0}\right) = -\frac{E_a}{nRT} + \frac{E_a}{nRT_0} \quad (3)$$

with a_0 the mass gain rate at some reference temperature T_0 .

If the rehydroxylation-related mass, m_{RHX} , gained over the lifetime of the ceramic can be estimated together with a suitable effective lifetime temperature, T_{ELT} (see Hall et al. 2013), then using the Arrhenius temperature dependence to estimate the rehydroxylation rate at the ELT, $a(T_{ELT})$, the age of the ceramic follows from rearrangement of *equation (1)*:

$$t = \left(\frac{m_{RHX}}{a(T_{ELT})}\right)^n, \quad [n = 4] \text{ (Wilson et al. 2009; 2012)} \quad (4)$$

2.2 Simulation Approach and Application

Three groups of simulations were run to examine STETE effects: (a) brick cooling effects, (b) pot cooking effects, (c) dating trial effects. The first two groups are entirely simulation based but use parameters for the ceramic behaviour that are from experimental work (Barrett 2015, 2017a). The third group of simulations is applied to samples (described below) tested in the dating trials of Barrett (2015, 2017a, 2017b) and uses a combination of both known and hypothetical STETEs from the samples' temperature histories to examine how these short term events may have affected the dating trial results.

Simulation of the mass gain for a particular temperature history profile was carried out using a step change approach (Barrett 2013; Hall et al. 2013) and the RHX equations of Wilson et al. (2009; 2012), see *Appendix A*. These were run in *MATLAB R2012a* using custom code and experimentally derived values of RHX mass gain rates and activation energies (Barrett 2015, 2017a). It has previously been shown that the mass gain behaviour is better described by a $t^{1/n}$ based equation, with $1/n$ potentially varying from 1/6-1/2 dependent on the sample (e.g. Barrett 2017a, 2017c; Le Goff and Gallet 2014, 2015b). For the present exploratory set of experiments $1/n$ was generally restricted to a value of 1/4 predominantly because it sits in the middle of the typical range of values expected and to a lesser extent because it is the original value used by Wilson et al. (2009, 2013); this also permits findings from the brick cooling experiment to be discussed more directly in relation to the positive results of Wilson et al. (2009) in which four of five sample materials were brick. For the dating trial tests, where $1/n$ estimates for individual samples have previously been made (Barrett 2017c), the effect of using the $t^{1/n}$ model with sample specific values was also explored.

Before the effects could be simulated, temperature profiles for each STETE were required. Heating and cooling temperature profiles were generated using *MATLAB* and Newton's law of cooling/heating (Arpaci et al. 2000) of the general form:

$$T(t) = T_0 \pm (T_i - T_0)e^{-bt} \quad (5)$$

where for a heating (-) or cooling (+) sample, $T(t)$ is the temperature as a function of time, T_0 is the temperature of the environment (final temperature the sample is cooling/heating towards), T_i is the initial temperature of the sample, and b is a constant that describes the rate of heating or cooling (referred to in text as the heating/cooling coefficient).

For simulation group (c), data obtained from cooling temperature profiles obtained experimentally was used in selecting suitable heating/cooling coefficients (see Barrett 2015 for details on collection of these profiles). For (a) and (b), hypothetical temperature profiles were generated, but in consideration of the experimental data from Barrett (2015; 2017a).

2.3 Brick Cooling Effects

The effect post manufacturing cooling of brick might have on ages estimates using were explored by generating the fractional mass gain of the ceramic for a range of cooling durations (6, 12, 18, 24 hours), corresponding to varying the cooling coefficient from $0.0189\text{--}0.0064\text{min}^{-1}$ (see *Figure 1* for cooling temperature profiles), followed by a range of aging durations (50–450 years) during which the brick has a constant temperature of 10°C . This was examined using activation energies of $60\text{--}200\text{kJ/mol}$ and for a typical fractional mass gain rate of $0.00005\text{hr}^{-1/4}$ at 10°C (based on typical values from Barrett 2015, 2017a). Age estimates were carried out using the fractional mass gain simulations but under the assumption of an ELT of 10°C (i.e. neglecting the STETE event), then compared with the actual ages, providing an age discrepancy (difference between the two ages) or additional age, t_{stete} , as a function of cooling duration, activation energy, and age of the ceramic. For this exploration, a maximum temperature to which RHX can proceed of 80°C was chosen (see *Discussion* regarding the selection/uncertainty in this maximum temperature).

2.4 Pot Cooking Effects

The effect the use of pottery in cooking/heating could have on ages estimates were explored by generating the mass gain of a pot for two main temperature profiles (cooking cycles):

a) Stewing - a 3 hour cycle consisting of heating the pot from 10°C to 70°C (approx. 45 minutes), followed by a dwell time of 1 hour, then cooling down to 10°C (approx. 40 minutes, the remainder of the 3 hour cycle corresponding to 10°). A cooling/heating coefficient of 0.112min^{-1} (average value of samples from Barrett 2015) was used, see *Figure 1*.

b) Boiling - a two hour cycle consisting of heating the pot from 10°C to 120°C (approx. 8 minutes) and then cooling down to 10°C (approx. 40 minutes, again any remaining time in the 2 hour cycle corresponds to 10°), with a cooling/heating coefficient again of 0.112min^{-1} ; the dwell time for this profile is irrelevant as the RHX process will proceed to a maximum temperature (see *Discussion, Section 4.1*), assumed to be much less than 120°C – in this case

70°C was selected, above which the temperature profile is not used, see *Figure 1*. Therefore only the heating and cooling portions are used with no need for any gap between.

Using both high (160-180kJ/mol) and moderate (100-120kJ/mol) activation energies and a fractional mass gain rates of $0.00005\text{hrs}^{-1/4}$, the fractional mass gain was generated for 1 week at 10°C followed by N cooking cycles (for either *stewing* or *boiling* and for $N = 1\text{-}300$ cycles). Age estimates were again carried out using the mass gain simulations under the assumption of an ELT of 10°C (i.e. neglecting the STETE event), then compared with the actual ages, providing an additional age, t_{stete} , for each cooking cycle type, as a function of number of cooking cycles and activation energy.

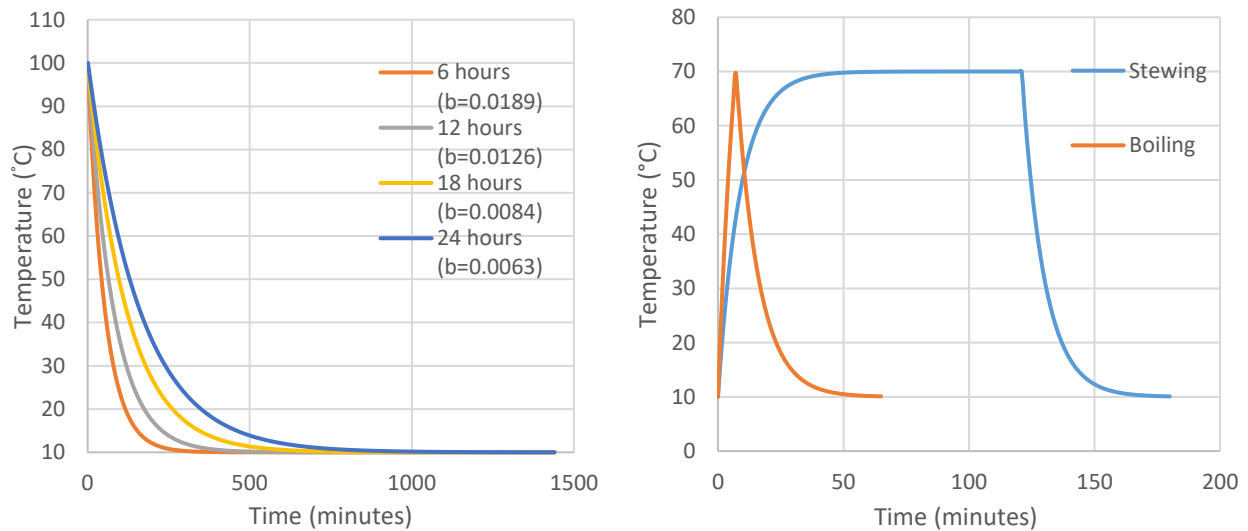


Figure 1: Temperature profiles used in (left) brick cooling and (right) pot cooking effect simulations. For pot cooking profiles, differences in the rate of heating and cooling are due to the *Boiling* cycle being generated under heating conditions of exposure to a higher temperature of 120°C (as opposed to 70°C) for *Stewing*. For the *Boiling* cycle, the temperature profile is edited to only include the portion relevant to RHX max gain, i.e. below 70°C.

2.5 Dating Trial Tests

The dating trial tests examined the possible effects of four STETE events that occurred during the lifetime of archaeological ceramics tested as part of an associated dating trial (Barrett 2017a, 2017b, 2017c).

In the associated dating trial, a dating methodology (a component based approach that is significantly modified from the method of Wilson et al. 2009, 2012) was applied to a sample set consisting of 18 samples but only 11 and 12 (dependent on application of a $t^{1/n}$ or $t^{1/4}$ model, respectively) of these had mass gain properties that permitted age estimations to be made (see Barrett 2015, 2017a, 2017b for method and sample details). These were all post-medieval brick samples, from Ireland and of known age (historical sources), to which a suite of characterization methods were applied (XRD, FTIR, p-XRF, petrography, BET analysis, see Barrett 2015 for full details). These bricks were likely fabricated from local residual/boulder clay (rich in quartz and feldspars and generally low or negligible in calcium content) and all showed signs of having been well-fired above 850°C (presence of high temperature phase transitions in minerals, e.g. cristobalite, spinel, mullite); temperatures approaching and above 1000°C are also likely for several, evidenced by high levels of vitrification (bloating/melting) under petrographic analysis. These samples also had notably lower surface area ($< 5\text{m}^2/\text{g}$) than the more problematic samples that could not be dated.

In brief, the dating methodology consisted of the following main sequence of events: sample preparation and pre-drying; drying at 130°C for 2 months to remove all capillary and loosely bound moisture; post-drying mass gain measurements, featuring the aging (at three different temperatures) and weighing of samples in controlled environmental conditions over a period of two months; reheating at 500°C to dehydroxylate the samples; post-reheating mass gain measurements, again featuring aging (at three different temperatures) and weighing of samples in controlled conditions over two months; data analysis and age estimation. Temperature histories were also constructed for each sample but these were limited to using only surface air temperatures (SAT) records in the locality of the samples retrieval context (Barrett 2015, 2017a for full details). These temperature histories permitted simulations to be made of the expected rehydroxylation mass gain across the lifetime of the ceramic (which in turn could be compared with the measured rehydroxylation mass gain estimated from mass gain experiments). Given that the age of the ceramic was known, this simulated rehydroxylation mass was used to estimate an effective lifetime temperature (ELT) through use of *Equation 4* and an understanding of the temperature response of the rehydroxylation rate from mass gain experiments.

The present work examines how four STETE events, not considered or treated in the associated dating trial, can affect the age estimations; in that regard, this work presents the age estimation implications of using an alternative and more detailed temperature history. The four events are as follows: (a) initial cooling of the ceramic post original firing (i.e. production); the pre-drying stages that involved (b) two days held at 60°C and (c) a more prolonged period (15 days) at 77-79°C, and (d) 60 heating/cooling cycles during removal from the oven for balance measurements while drying (130°) to constant mass. Aside from the brick cooling event that occurred immediately after the brick was fired, the remaining STETE events are recent features of the dating methodology that was applied. The two pre-drying events, (b) and (c), were conducted in a drying cabinet in order to remove wet-cutting related moisture (from sample preparation) and bulk/capillary moisture more slowly than would be the case at higher temperatures (where more rapid moisture loss might cause associated structural changes in the ceramic matrix; issues with this are discussed in Barrett 2015). The 60 heating/cooling cycles resulted from periodic removal from the oven for weighing of samples during unexpected and prolonged drying at 130°C (see Barrett 2017b).

A temperature profile for each event was required. For events (b) and (c), the cooling and heating part of the profiles were not deemed necessary as their mass gain contributions are insignificant with respect to that of the prolonged period sitting at maximum temperatures (60°C, 77-79°C). For event (d), heating and cooling curves were generated using the methods in *Section 2.2* and the average heating/cooling coefficient ($0.112 \pm 0.006 \text{ min}^{-1}$) obtained from modelling all experimentally obtained cooling profiles. Cooling profiles were obtained by placing beakers of sample material (granulated as used in mass gain experiments and as would have been the case for event (d)) in an oven at 150°C for longer than 1 hour to ensure thermal equilibrium. Once removed, surface temperature probes were immediately placed centrally into the granules and the temperature was logged (*Grant Squirrel 1000 Series* datalogger, $\pm 0.2^\circ\text{C}$) as the sample cooled to laboratory conditions (typically 1.5 hours). For event (a), the heating/cooling coefficients used for generating the cooling curve profile were modelled from the cooling response of a whole test brick (Chester Red brick, coefficient = 0.0192 min^{-1}).

With no evidence available to indicate what upper temperature rehydroxylation can proceed to (see *Discussion*), a lower estimate of 80°C and a higher estimate of 95°C were selected. For event (c) a lower estimated of the cabinet temperature of 77°C and 79°C upper estimate were used (the range of uncertainty in the temperature of the cabinet).

To estimate the cumulative additional mass gain of all four STETE effects, over that expected by the ELT alone, the simulated lifetime rehydroxylation mass gain based on the SAT temperature history alone (used in the ELT estimation, discussed earlier) was used as the initial mass (described in Barrett 2015); this mass is equivalent the rehydroxylation mass gain, m_{RHx} , calculated from *Equation 4*, for a ceramic of known age, t , with a rehydroxylation rate, a_{ELT} , and using an ELT that is obtained from the SAT temperature history alone. Then, in sequence, each of the above effects was added (generated) onto this mass. The ordering of events bears no effect on the total mass gained; this has been demonstrated by Hall et al. 2013 (the author has also tested this through rearrangement of events in simulations). The additional mass gain due to STETE events, m_{STETE} , was obtained by subtracting the total simulated mass of the temperature history and STETE events from the mass gain due to temperature history (ELT) alone (extended in length by the period of duration of STETE events).

The STETE event effect simulations were carried out for two sequences of the events:

1. Moderate: temperature history, cooling ceramic (80°C max), 2 days 60°C, 15 days 77°C, 60 heating and cooling cycles (80°C max)
2. Strong: temperature history, cooling ceramic (95°C max), 2 days 60°C, 15 days 79°C, 60 heating and cooling cycles (95°C max)

The additional age, t_{STETE} , was calculated from the difference in age estimates calculated using the mass gain due to temperature history (ELT) alone and with m_{STETE} added. Ages were calculated using the equations in *Section 2.1*. This additional age, t_{STETE} , was then compared with the age discrepancies, t_{out} , observed between the known age of the ceramics and the age estimates from the associated dating trial (Barrett 2015, 2017a; again the ELTs used in the dating trial were based on SATs alone).

The STETE effects were calculated comprehensively for the $t^{1/4}$ model and to a less detailed level for the $t^{1/n}$ model for comparison.

3. Results

3.1 Brick Cooling Effects

The fractional mass gain (FMG) during cooling (and for a period up to 24 hours) shows considerable increases with activation energy and to a lesser extent the cooling duration, *Figure 2*. A continuation of these curves over much longer periods (1-450 years), *Figure 3*, demonstrates the magnitude of the additional mass gained as well as a clear curvature in the data when expressed as a function of $time^{1/4}$. The effect additional mass gain has on age estimates (calculated using the assumption of an ELT of 10°C) can be significant, *Figure 4*, with additional ages from 23 years (160kJ/mol) to 111 years (180kJ/mol) to 541 years (200kJ/mol); the effect is most pronounced in the temperature range 80-65°C. For activation energies < 150kJ/mol, *Figure 5*, age calculations are likely to be overestimated by up to a decade, but above this value the additional age rises considerably as a function of activation energy and to a lesser extent cooling duration. Above 180kJ/mol, additional ages in excess of 50 years occur. Uncertainty in the original cooling conditions can also lead to considerable variation in the possible magnitudes of the brick cooling effects, e.g. for 180kJ/mol, varying from approximately 40-110 years for the cooling durations used.

The additional age is equivalent to a time-offset type effect (Barrett 2013); it has added a fixed age to the ceramics by the end of the event (cooling) and this fixed quantity does not change, remaining independent of the subsequent lifetime of the ceramic.

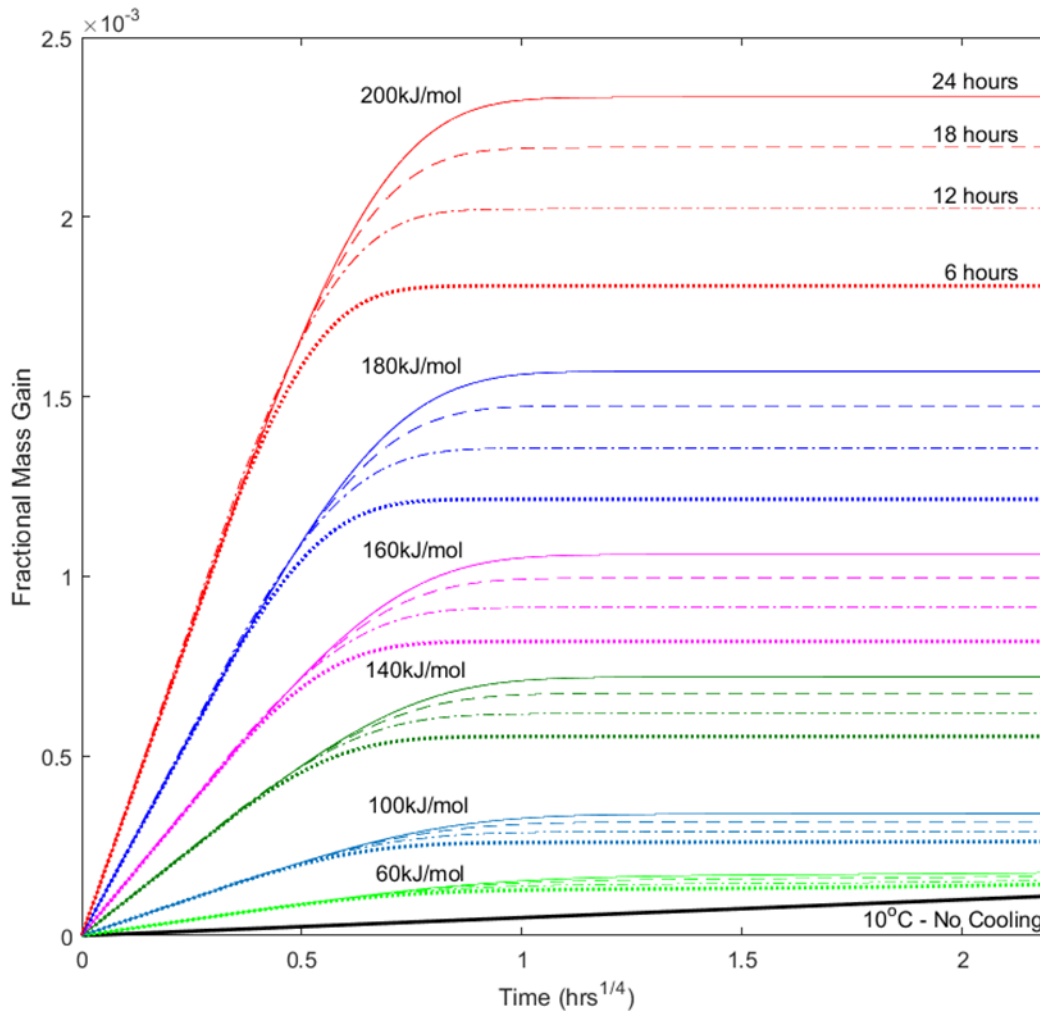


Figure 2: Fractional mass gain curves, as a function of $\text{time}^{1/4}$, during cooling of brick with durations of 6-24 hours and for a range of activation energies, 60-200 kJ/mol (for a reference RHX fractional mass gain rate of $0.00005 \text{ hrs}^{-1/4}$ at 10°C). The solid black line represents the fractional mass gain of a ceramic that has been instantaneously cooled to 10°C following firing and subsequently continues aging at that temperature (an idealised condition that is extremely unlikely for archaeological ceramics).

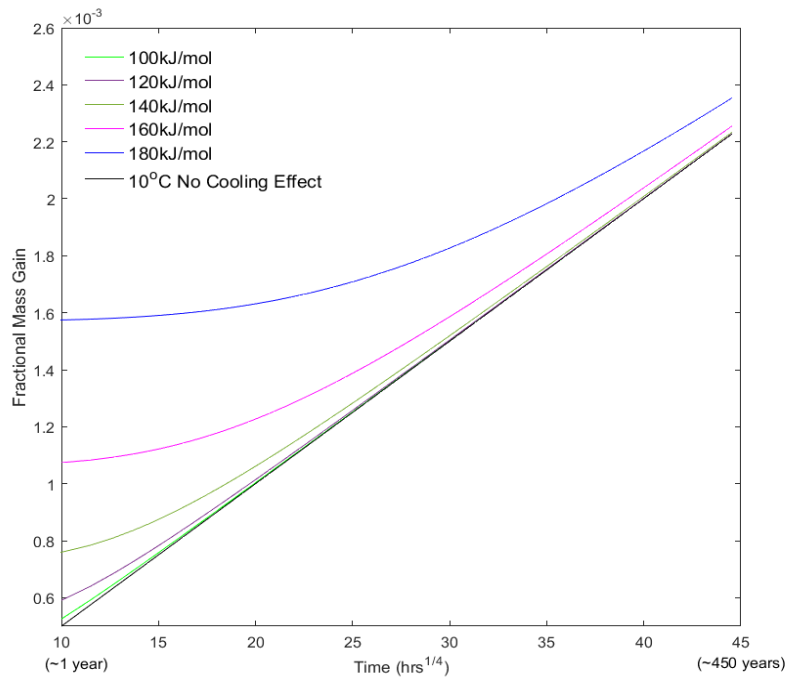


Figure 3: Fractional mass gain curves, as a function of $time^{1/4}$, following cooling of a brick (24 hour duration), for a range of activation energies, 100-180kJ/mol (for a reference RHX fractional mass gain rate of $0.00005\text{hrs}^{-1/4}$ at 10°C), over the period 1-450 years (such curves would be expected of a structural brick that is positioned exposed to a relatively constant temperature during its lifetime, for example in a wine cellar). The solid black line represents the fractional mass gain of a ceramic that has been instantaneously cooled to 10°C following firing and subsequently continues aging at that temperature.

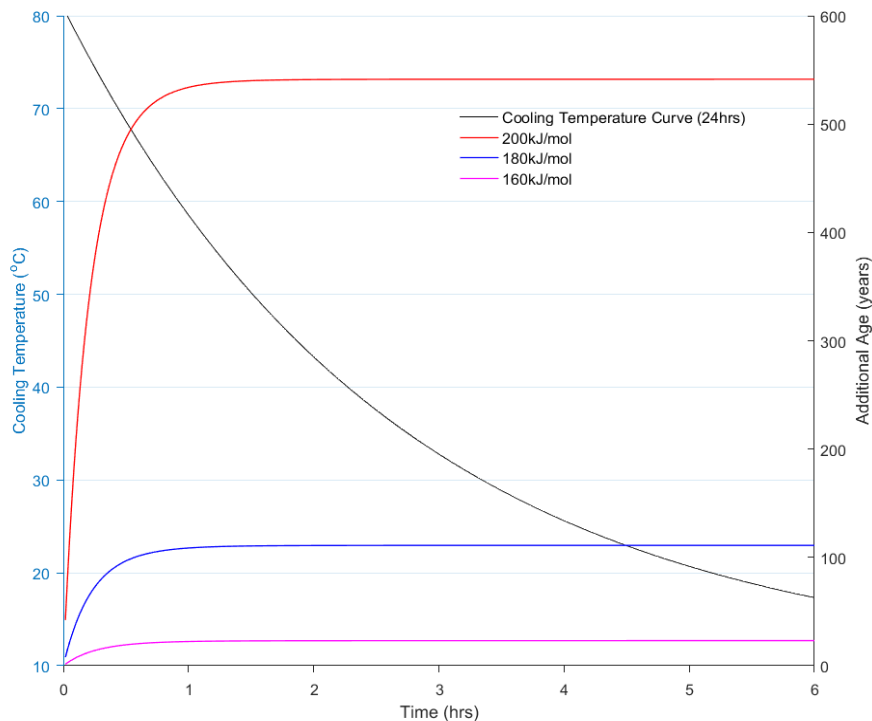


Figure 4: Additional age added to bricks of activation energies 160-200kJ/mol as a function of cooling time/temperature (for total cooling duration of 24 hours). The additional age represents the difference in age estimates that would be obtained (assuming an ELT of 10°C) between a brick which has experienced gradual cooling and one which has experienced instantaneous cooling.

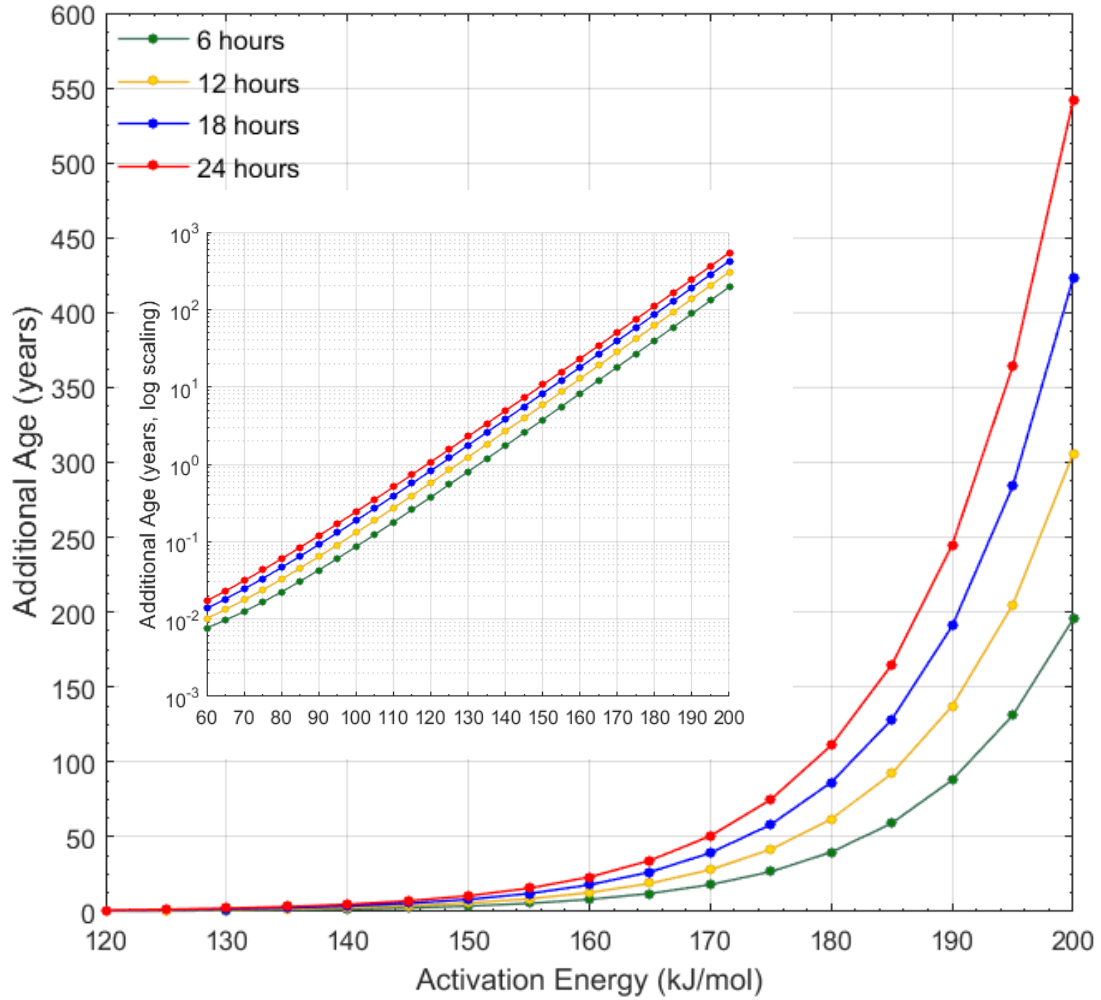


Figure 5: Additional age caused by brick cooling over durations of 6-24 hours and for activation energies of 60-200 kJ/mol (presented inset using log scaling). Main plot presents the region 120-200kJ/mol over which effect is most pronounced. For a fractional mass gain rate of $0.00005\text{hrs}^{-1/4}$.

3.2 Pot Cooking Effects

A stepwise increase in additional age with each *stewing* or *boiling* cycle can be observed, *Figure 6* and *Figure 7*. The additional age increases by a fixed quantity with each cycle despite the fractional mass gain increase diminishing; this increase in age is independent of the time at which the cycle occurs. The additional age for any number of cycles, N , is simply N times that for a single cycle.

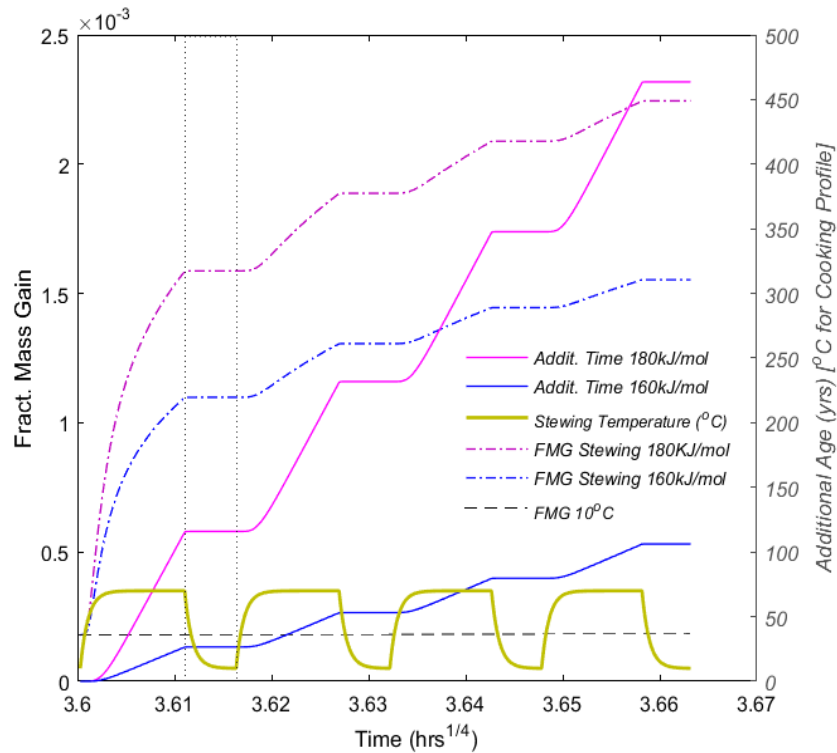


Figure 6: Fractional mass gain and additional age caused by 4 pot stewing cycles (commencing following 1 week of aging at 10°C) for activation energies of 160 and 180 kJ/mol. For a fractional mass gain rate of $0.00005 \text{ hrs}^{-1/4}$ at the reference temperature of 10°C. Also included are the temperature profile of the cooking cycles and the fractional mass gain with no cooking effect.

The magnitudes of the effects are far more pronounced for stewing (of the order of 26 – 116 years per cycle) than for boiling (7 months – 2.4 years) on account of the hour long dwell time. The age added per cycle increases considerably with activation energy, *Figure 8*; above 120kJ/mol additional ages in excess of 1 year per cycle would be expected, increasing to 506 years at 200kJ/mol. For boiling, the effects are much reduced with a single cycle adding an additional age of 1 year for activation energies in excess of 170kJ/mol. For a pot used for 100 cooking cycles, say 50 boiling and 50 stewing, the additional age that will be added (assuming the temperature cycle profiles used are appropriate) for a

very low activation energy, 80kJ/mol, is 5 years (50 x 4 weeks + 50 x 1.2 weeks), for a moderate activation energy, 140kJ/mol, is 308 years (50 x 6 years + 50 x 2 months), and for a high activation energy, 180kJ/mol, is 5920 years (50 x 116 years + 50 x 2.4 years). As for brick cooling, this additional age is independent of the actual age of the ceramic.

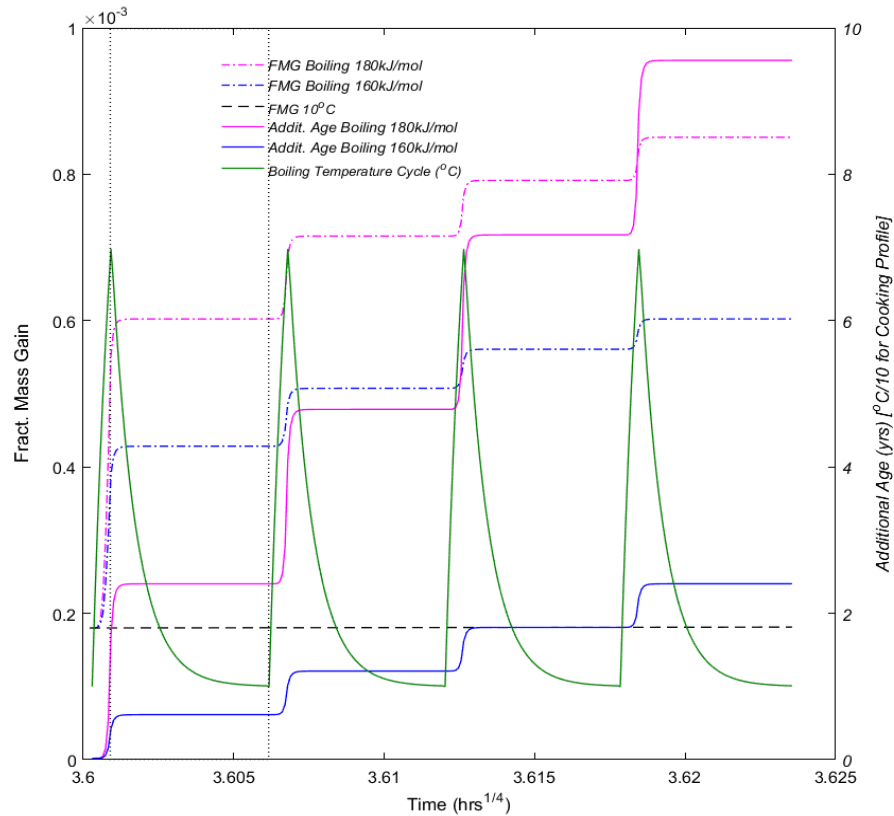


Figure 7: Fractional mass gain and additional age caused by 4 pot boiling cycles (commencing following 1 week of aging at 10°C) for activation energies of 160 and 180 kJ/mol. For a fractional mass gain rate of $0.00005 \text{ hrs}^{-1/4}$ at the reference temperature of 10°C. Also included are the temperature profile of the cooking cycles and the fractional mass gain with no cooking effect.

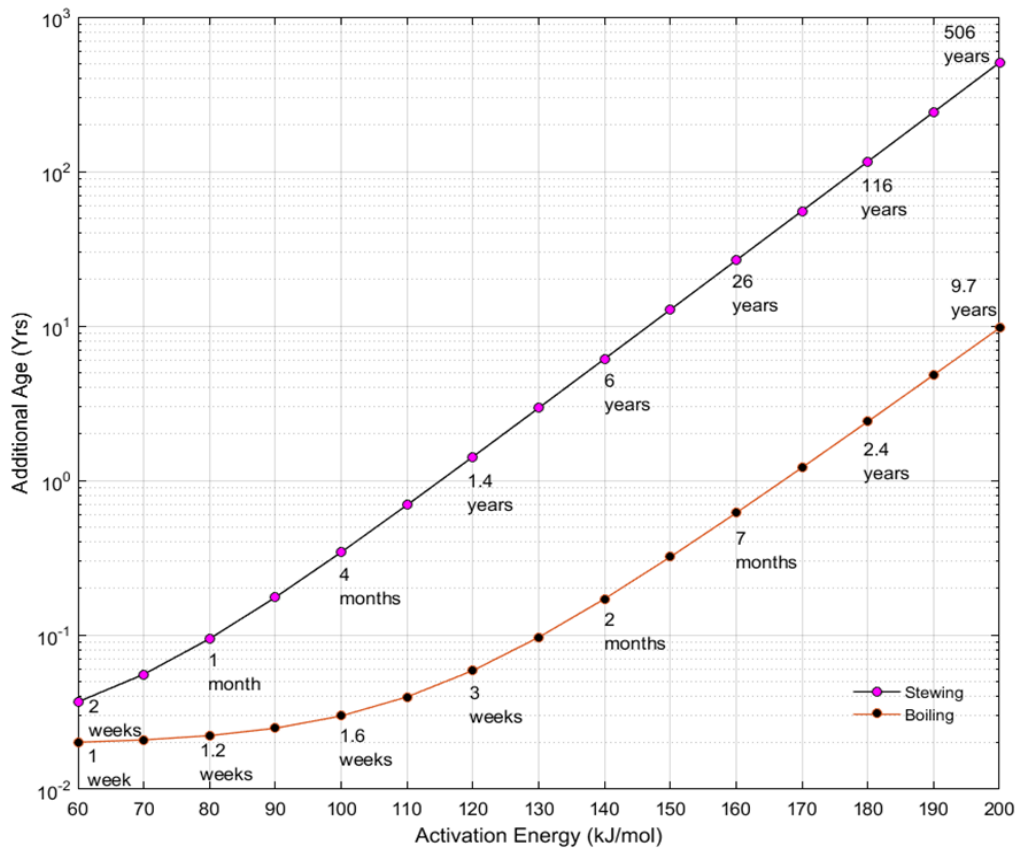


Figure 8: Additional age added to ceramics as a function of activation energy and for a single cooking cycle of either stewing or boiling. Age axis plotted to logarithmic base 10.

3.3 Dating Trial STETE Effects

The cumulative fractional mass gain effects from simulations of dating trial STETE effects are presented in *Table 1*. These results are for a $t^{1/4}$ model. The potential extra age, t_{STETE} , caused by the extra mass gain of these events are presented, together with the age the dating calculations were out by (see Barrett 2015 for full dating results), t_{out} , included for comparison. In terms of the order of magnitude of the age effect, strong similarities are observed between the STETE effects and discrepancies in the dating calculations. Also clear from the tables is the strong relationship between the activation energy and the magnitude of STETE effects; for activation energies under 100kJ/mol the effect is minor for most STETE events. The most significant contributor of all the STETEs is the 15 day 77-79°C event but for high activation energies all STETE events can potentially add significant age to the ceramic.

442 Table 1: Extra age, t_{STETE} , caused by STETE effects, using *moderate* (Mod.) and *strong* (Str.) conditions.
443 t_{out} =difference between known age and age estimates from dating trial (Barrett 2017a). BC (80) = Brick Cooling
444 (80=max. RHX temp.). 2d60=2 days heating at 60°C. 15d77=15 days at 77°C. 60c80=60 heat/cool cycles with max.
445 temp of 80°C.

Mod.	E_{aRHX} (kJ/mol)	t_{out} (years)	t_{STETE} BC (80) (years)	t_{STETE} BC (80) +2d60 (years)	t_{STETE} BC (80) +2d60 +15d77	t_{Stete} BC (80) 447
						+2d60 448 +15d77 +60c80
Ann	132.15	570	0.8	22.8	1584.8	1614.8
Esp	76.61	127	0.0	0.7	20.8	21.2
Nic	204.35	55567	213.6	2112.8	464981.0	475057.0
Mac	294.94	555199181	214176.5	611495.0	453734399.0	467734684.0
Ria	179.31	153481	32.5	463.7	69083.0	70483.0
Rat	182.90	1752185	39.2	531.6	83814.0	85526.0
Cal	83.33	2478	0.0	1.1	35.8	36.6
Joy	89.08	-13	0.0	1.7	59.4	60.6
Cau	99.86	129	0.1	3.6	149.1	152.0
Bel	40.23	469	0.0	0.1	1.5	1.2
Tur	155.34	47823	5.8	116.4	11815.0	12044.2
Ted	103.64	-124	0.1	4.1	177.1	180.5
Str.	E_{aRHX} (kJ/mol)	t_{out} (years)	t_{STETE} BC (95) (years)	t_{STETE} BC (95) +2d60 (years)	t_{STETE} BC (95) +2d60 +15d79	t_{STETE} BC (95) 456
						+2d60 457 +15d79 +60c95 458
Ann	132.15	570	4.5	26.4	1588.4	1696.0
Esp	76.61	127	0.0	0.8	24.0	24.5
Nic	204.35	55567	3112.9	5014.1	695380.0	780032.0
Mac	294.94	555199181	10819208.0	11223588.0	818105403.0	1145421875
Ria	179.31	153481	335.6	767.1	98221.0	107014.0
Rat	182.90	1752185	425.8	918.5	120029.0	131249.0
Cal	83.33	2478	0.1	1.2	42.0	43.5
Joy	89.08	-13	0.1	1.8	70.4	72.9
Cau	99.86	129	0.3	3.9	180.7	187.7
Bel	40.23	469	0.0	0.1	1.6	1.3
Tur	155.34	47823	43.1	153.7	16007.9	17091.2
Ted	103.64	-124	0.4	4.3	216.2	224.9

The effects were also explored for the $t^{1/n}$ to a lesser extent. The STETE effects on the ages are presented in *Table 2* for several sets of conditions. Again, a strong contribution to the age discrepancies, t_{out} , is possible for high activation energy samples, particularly due to the 15 day 77-79°C STETE events.

Table 2: The STETE effects on the $t^{1/n}$ ages. t_{out} is the difference between the estimated age from dating trials (Barrett 2017a) and the known age. t_{STETE} is the additional age the STETE event would contribute (based on the additional mass the event adds to the simulated mass gain of the ceramic over its lifetime). The STETE events are as follows: BC80 = brick cooling with maximum RHX temperature of 80°C, 2d60 = 2 days at 60°C, 60C80 = 60 heating/cooling cycles with maximum RHX temperature of 80°C. Note that yrs=0 corresponds to an additional age of <0.5 yrs.

$t^{1/n}$	E_{aRHX} (kJ/mol)	Known Age (yrs)	t_{out} (yrs)	t_{STETE} BC80+2d60+60C80 (yrs)	t_{STETE} 15d77 (yrs)	t_{STETE} 15d79 (yrs)
Ann	95.67	110	-1	5	89	110
Esp	78.86	141	448	1	24	28
Nic	270.01	398	1023960	2128225	72125062	122320699
Mac	232.53	228	9148685	104272	3875769	6108360
Ria	119.10	339	4530	23	611	771
Rat	100.17	245	4665	6	131	159
Cal	56.86	182	12	0	4	5
Joy	82.77	412	-233	3	35	41
Bel	23.51	395	3995	0	1	1
Tur	86.10	229	194	2	47	56
Ted	55.80	339	-321	0	4	5

4. Discussion

4.1 Maximum RHX Temperature

To provide more accurate estimates of the magnitude of STETE effects on the estimated ages of ceramics, an understanding of the maximum temperature to which RHX proceeds is necessary. This temperature, at which removal of moisture from the surface of the ceramic becomes dominant and begins to restrict the probability of rehydroxylation, is poorly understood. Barrett (2013) provided a rough estimate, based on considerations of *time-offset* effects and curvature in samples (assuming a $t^{1/4}$ model), that RHX mass gain had commenced in the temperature range 56-58°C. However, this work pre-dated a growing body of work (e.g. Bowen et al. 2011, 2013; Le Goff and Gallet 2014a, 2015a, 2015b; Barrett 2015, 2017c) that argues strongly for the mass gain behaviour being better described by a $t^{1/n}$ model. Hence, if the (positive) curvature in Barrett (2013) features a strong component characteristic of the ceramic, then the *time-offset* effect must be less and the RHX commencement temperature should also be higher than 56-58°C. In Barrett (2015, 2017a, 2017c), a large set of samples exhibited typical mass gain behaviour up to 45°C and Wilson et al. (2009) have observed normal (approximately $t^{1/4}$) behaviour at 50°C. In terms of a limiting temperature, Bowen et al. (2011) did have issues with the mass gain behaviour of a sample aged at 80°C (behaviour was poorly described by a generalised $t^{1/n}$ model) which might be telling. Also, Gallet and Le Goff (2015) found that after heating samples at temperatures as low as 60°C for 5 hours, subsequent mass gain was observed to proceed as a function of $t^{1/4(n)}$; this suggests the removal of physisorbed and possibly (weakly) chemisorbed water with which it seems likely that the continuation of RHX mass gain processes might be disturbed.

Indeed, if the process of chemisorption/RHX of water molecules (or hydroxyls) requires some level of physisorbed moisture to be present (i.e. an increased residence time of water molecules near reactive RHX sites), then it can be assumed that chemisorption/RHX mass gain will have ceased by 105-110°C. The works of Gallet and Le Goff (2015) above and Barrett (2015, 2017c) provide evidence and strong arguments for the removal of both physisorbed and chemisorbed moisture at these temperatures; this chemisorbed moisture is distinct from, and removed at a lower temperature than, rehydroxyls which are likely removed above 300°C (see Barrett 2017c for discussion). TG-MS data from Barrett (2015, 2017c) shows a maximum rate of removal of physisorbed water by 70°C in 10 out of 12 well behaved samples; this might be indicative of a maximum RHX temperature, provided the assumption that the presence of physisorbed water is necessary for RHX to proceed has validity.

Therefore, the best evidence available might suggest RHX mass gain will cease or be limited at temperatures of 60-70°C. Yet the evidence is not entirely convincing and requires more investigation. The results of the present work should be considered in light of this; various limiting temperature (70-95°C) are defined and used in order to examine the potential effects that might be expected from STETEs but, in reality, the limiting maximum RHX temperature is not yet known and may be sample specific. Therefore, the simulation results can only be taken as a guide to the possible magnitudes of the additional age issues raised by certain STETEs.

4.2 Brick Cooling Effects and Pot Cooking Effects

Brick Cooling Effect

Additional mass gained during cooling of a brick can add considerable additional age to a ceramic if unaccounted for. The strong dependence of this additional mass gain due to STETEs on the activation energy is most clearly demonstrate in *Figure 2* and *Figure 5*. For activation energies below 150 kJ/mol the magnitude of the effect can be considered limited, but for values > 150kJ/mol additional ages of at least decades will be added to the ceramic and can amount to hundreds of years under certain conditions (> 185kJ/mol). In order to date bricks with high activation energies then, this effect needs to be taken account of. Knowledge of the methods of firing can become important as variation in the duration of cooling can greatly affect the quantity of additional age added, *Figure 2* and *Figure 5*. A greater understanding of the maximum RHX temperature is needed also as, demonstrated in *Figure 4*, the most significant amount of mass gain occurs in the early periods of cooling during which the temperature is at its highest (for example in the 1st half hour, between 80-65°C approximately 85-95% of total additional age will have been added). If the maximum RHX temperature is less than 65°C the BCE effect could be of limited concern. It also needs to be stated this effect can apply to all ceramics that have cooled slowly during initial firing, although for thin walled vessels, with a proportionally higher surface area to bulk volume ratio, cooling is expected to be considerably more rapid (greater heat flow to total heat capacity ratio).

An important note in consideration of the brick cooling effect relates to the dating results of Wilson et al. (2009) which included tests on Roman paving brick, a brick from King Charles II building, a clay brick from Whitefriars Priory site, and a Chester Red clay brick (i.e. four of the five different materials dated were brick, the other being tile). An

activation energy of 182 ± 5 kJ/mol was estimated for these samples. If this is the case, additional age of the order of at least 40-110 years due to brick cooling effects might be expected in the dating results, *Figure 5*. However, no significant age discrepancies were encountered (see *Figure 4* of Wilson et al. 2009). This only adds to the issues raised regarding this work by Le Goff and Gallet (2015a) and Barrett (2015).

Pot Cooking Effect

The results in *Figures 6-8* make it clear that where pots/ceramics have been used in functions involving heating, there is the potential for STETE related effects to be considerable. The magnitude depends greatly on the cooking profile, compare *Figure 6* and *Figure 7*, and also on the number of cycles the pot is likely to have gone through during its lifetime. For a single *stewing* cycle, the additional age added becomes more problematic (i.e. greater than 1 year) for activation energies exceeding 120kJ/mol, whereas for the *Boiling* cycle, activation energies of 170kJ/mol are required for a similar level of additional age, *Figure 8*. For *Stewing*, high activation energy samples are very problematic, with a single cycle capable of contributing 116 years (activation energy of 180kJ/mol). Of significance, is that the total additional age added is simply a multiple of the number of cycles times the additional age for a single cycle, see *Figure 6* and *Figure 7*; the additional age of a single cycle is independent of the point in the ceramics history at which the cycle occurs (this has previously been expressed in Hall et al. 2013).

For pots used on a daily basis in cooking, several months of use can contribute considerably to the estimated age of the ceramic. For example, a pot used for 180 boiling cycles (daily use for six months) and with a moderate activation energy of 120kJ/mol will add approximately 10 years to the age of the ceramic. If the same pot has an activation energy of 180kJ/mol, the additional age contribution rises to 432 years. If the pot is instead used with something akin to the *stewing* cycle, then the additional age for an activation energy of 120kJ/mol is 252 years, and for an activation energy of 180kJ/mol is approximately 21000 years. Again, the magnitudes depend on the cycle profile, on the thermal properties of the ceramic, and on the maximum RHX temperature, but the simulations serve to clearly demonstrate that pots used in cooking (or to be more prudent, archaeological ceramics with evidence of food residues still present) that have even moderate activation energies, say >120kJ/mol, must be completely avoided in dating trials. It is conceivable that all cooking pots should be avoided should the maximum RHX temperature be significantly higher, however, as discussed earlier, the limit of this maximum temperature requires further research.

4.3 Dating Trial STETE Effects

STETE effects on dating trials were examined under *moderate* and *strong* conditions or maximum RHX mass gain temperature, up to 80°C or 95°C, respectively. The effects on estimated ages, t_{stete} , are considerable, *Table 1-3*. The brick cooling effect adds very little extra age to many samples (< 1 year for *Ann*, *Esp*, *Cal*, *Joy*, *Cau*, *Bel*, *Ted*) but as the activation energy increases beyond 150kJ/mol the effects become more pronounced, adding 43 years to *Tur* (155kJ/mol), 426 years to *Rat* (183kJ/mol), 3112 years to *Nic* (204kJ/mol), and 10 million years to *Mac* (295kJ/mol) (all for the *strong* case but the *moderate* case is similar). Again, the brick cooling effect is problematic for high activation energy samples.

For the pre-drying stages, the two days at 60°C show similar trends with significant effects only for samples with activation energies exceeding 130-150kJ/mol (for example 20 years are added to *Ann*, 132kJ/mol). Heating at 77-79°C for 15 days produces an extreme level of additional age for some samples and, significantly perhaps, the extra age is of a similar order to that of the age discrepancy, t_{out} , between the estimated and known ages obtained in Barrett (2015, 2017a). The magnitude of the effect is far too great for *Nic* and too small to explain the major issues with *Cal* or *Bel*. The results certainly highlight that (pre-)drying of samples at lower temperatures (60°) or inadequately high temperatures (75-80°C) could both have notable and problematic effects for the RHX dating of samples. If RHX mass gain proceeds to these temperatures without restriction, then the agreement between the order of magnitudes of t_{stete} and t_{out} suggest that the pre-drying methodology employed in Barrett (2015) is flawed and has contributed to poor dating results in samples with higher activation energies. On the other hand, the similarity in magnitudes may be providing a demonstration that STETEs indeed have a real effect and RHX mass gain does proceed to 70-80°C, at least. This also has implications for any archaeological ceramics or museum pieces which have undergone drying at elevated temperatures following excavation; their use in RHX dating trials should be avoided.

After the 15 days at 77-79°C event, the effect of 60 heating/cooling cycles has the greatest effect, with similar magnitudes of additional age contributed as those of two days at 60°C. Again, the effect is only considerable for samples with activation energies exceeding 130-150kJ/mol. In the dating trials (Barrett 2015), this heating/ drying was necessitated by the need for repeated measurements of the sample mass during drying; in future this could be avoided by the use of a thermo-gravimetric type drying setup.

The dating trial STETEs were only examined in detail for the $t^{1/4}$ model because many of the samples have activation energies high enough for significant effects to potentially occur; for the $t^{1/n}$ model (see Barrett 2015 for full details on activation energies and their estimation), the activation energies estimated were notably lower, see *Table 2*, with only *Nic* (which was problematic in its activation energy estimation) and *Mac* having activation energies $> 130\text{kJ/mol}$. Nonetheless, examination of *Table 2* makes it clear that for the $t^{1/n}$, despite a much less pronounced effect than for the $t^{1/4}$ model (largely due to lower activation energy estimates), the STETE derived additional age contributions can be considerable for certain conditions (15d77/79) yet near negligible for others (brick cooling, 2d60, 60C80), except where activation energies are high (*Nic* and *Mac*). Certainly for the $t^{1/n}$ model, the discrepancies in the age estimations, t_{out} , do not appear to be explained by STETE effects, t_{STETE} , to the same extent they might be for the $t^{1/4}$ approach. This does not imply that the $t^{1/4}$ model is more valid; instead, it demonstrates that there are considerable differences that occur depending on the $1/n$ value used and that in future RHX work where STETE modelling is required, and suitable temperature histories can be constructed, use of the ceramic specific $1/n$ value is recommended (a range of other complicating factors affecting the dating trial results are detailed and discussed in Barrett 2015, 2017a, 2017b).

5. Conclusion

Examinations were carried out into the potential effect short term elevated temperature events (STETEs), where the ceramic temperature exceeds 50°C , might have on age estimations using an RHX dating methodology. For simulations of the mass gained during cooling of bricks and of the mass gain by a pot under various conditions (e.g. activation energy, cooling time, maximum RHX temperature, no. of cycles, *stewing* and *cooking* cycle), it is demonstrated that considerable quantities of additional age can be added to the age of the ceramic, leading to a false estimate of the age if STETEs are unaccounted for.

For bricks cooling, the activation energy is a critical; for values exceeding 150kJ/mol , decades to hundreds of years can be added to the age estimate. Cooling duration is also shown to have a major effect and for high activation energies can be equally problematic. The need for careful interpretation of dating results carried out on bricks, or indeed ceramics which would have experienced slow cooling times following original firing, is concluded.

The extra age added to a pot on account of cooking (*stewing* and *boiling*) is highly dependent on the temperature profile of the cooking cycle, being more pronounced for conditions that involved stewing at high temperatures. The number of cycles adds additional age equal to a multiple of the additional age for a single cycle; for a pot that has been used frequently for both *boiling* and *stewing*, it is easy for additional age of the order of hundreds or even thousands of years to accumulate. The effect is also dependent on the activation energy of the ceramic, with values in excess of 120kJ/mol more problematic. In relation to RHX dating, pots/ceramics that might have been used for cooking/heating of foods should not be used in dating trials.

That STETEs might be a major contributor of issues with age estimation discrepancies in Barrett (2015) was also examined. For high activation energy samples, STETEs associated with original firing and experimental treatment of the ceramic are shown to be plausible sources of a large part of the age discrepancies observed when using a $t^{1/4}$ model; however, for a $t^{1/n}$ model, where activation energies are estimated to be lower, the contribution of STETEs is insufficient to explain the much of the age estimation discrepancy.

In all of the above, a critical factor is the maximum temperature to which RHX mass gain can proceed. This value is not well understood and may vary with the sample. The present work provides results arguing strongly for the need of a better understanding of this characteristic. Until this factor is better comprehended, RHX dating trials must be selective in the use, ideally, of samples with very well understood temperature histories, with low activation energies, free of signs of use in cooking or exposure to STETEs. They should also be designed with methodologies that avoid exposing the ceramic to any periods, even of short duration, at elevated temperatures.

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Appendix A: Step Change Approach

This iterative approach calculates the total mass gain at each additional time increment along the temperature history profile of a sample, and is described below for a profile of three sequential temperature periods T_0 , T_1 , T_2 , that are bound and separated by the times 0 , t_0 , t_1 , t_2 , *Figure A.1*.

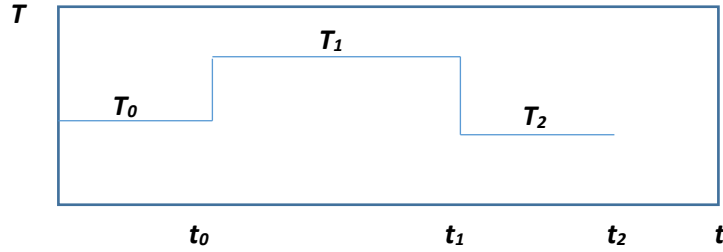


Figure A.1: Temperature history with three periods of different temperature.

The steps in simulating the total mass gain, m_0 , m_1 , m_2 , across this simple temperature history are as follows (see Barrett 2015 for further details on the equations used):

1. Calculate the mass gain rate, $a(T)$, at T_0 :

$$a(T_0) = a_{ref} \exp \left[-\frac{E_a}{4RT_0} + C \right] \quad (\text{A.1})$$

where $C = E_a/4RT_{ref}$, a_{ref} is a reference mass gain rate that has been measured at temperature T_{ref} , E_a is the activation energy.

2. Calculate the mass gain, $m(t)$, across T_0 :

$$m_0 = a(T_0)t_0^{1/4} \quad (\text{A.2})$$

3. Calculate the mass gain rate for temperature T_1 , as above using (1)

4. Calculate the effective time, t_0' , at the start of T_1 :

$$t_0' = (m_0/a(T_1))^4 \quad (\text{A.3})$$

which through use of (2) can be expressed as,

$$t_0' = (a(T_0)t_0^{1/4}/a(T_1))^4,$$

and through substitution of (1) reduces to,

$$t_0' = t_0 e^{\frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_0}\right)} \quad (\text{A.4})$$

This is the time it would take for mass gain m_0 to have occurred at temperature T_1 . Hence, the additional time, t_{stete} , added by this step, $t_0' - t_0$, is independent of mass gain rates.

5. Add the duration of T_1 , $t_1 - t_0$, to the effective time t_0' to obtain t_1'

$$t_1' = t_0' + (t_1 - t_0) \quad (5)$$

6. Calculate that total mass gain at the end of T_1 :

$$m_1 = a(T_1)(t_1')^{1/4}$$

7. Repeat steps 3-6 to calculate the mass gain at the end of T_2 .

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